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K.I. McRae and C.A. Waggoner

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Abstract

The design, function and application of a curved crystal graphite monochromator in X-ray diffractometry are reviewed. By further diffraction of the primary diffracted X-ray beam, the crystal removes unwanted radiation, including Kβ and other target lines and fluorescent or scattered radiation from the sample, with the result that signal-to-background ratios are significantly improved. Recorder scans and signal-to-noise data are presented for a variety of chemical compounds, including an ash deposit from a ship's boiler, to illustrate the effectiveness of the monochromator in the analytical application of X-ray diffractometry.

THE APPLICATION OF A CURVED GRAPHITE CRYSTAL MONOCHROMATOR TO X-RAY DIFFRACTOMETRY

INTRODUCTION

For most effective utilization of the information produced by x-ray diffractometry, at least partial monochromatization of the x-ray beam must be achieved. The degree of monochromatization required is largely dependent upon the complexity of the material being analysed. In some cases, elimination of only the Kβ line and continuous radiation may be sufficient, while the detection of a narrow bandwidth of x-radiation is often necessary. The monochromatization of the x-ray beam has several useful effects, but, generally, the function of a monochromator is the elimination of undesired radiation which may complicate the diffraction pattern and cause high continuous background.

The crystal monochromator, one of several methods of x-ray monochromatization, viz. beta filter, pulse height discrimination, Ross balanced (absorption edge) filters, acts as a narrow band-pass filter which can essentially isolate the Kα doublet and is, therefore, an efficient means of monochromatization. With this monochromator, it is possible to completely isolate the α_1 component of the Kα doublet if certain geometry requirements are achieved. However, this refinement is not necessary for the normal operation of the diffractometer, and is not pertinent to this investigation.

Crystal monochromatization has long been applied to x-ray diffractometry and spectrometry. Lang (1956), constructed and studied a quartz $(10\bar{1}1)$ crystal monochromator which was cut and bent to provide adequate focussing of the x-ray beam. A monochromator of a similar geometry, employing a LiF (200) crystal, was later developed by Ogilvie (Unpublished Data) and described in some detail by Koffman and Moll (1964). This design is available commercially and is marketed by the Advanced Metals Research Corporation as an adaptation to the Norelco (or Philips-Eindhoven) wide range goniometer. Canon (1965) demonstrated that a highly structured, pyrolytic graphite crystal could act as an efficient monochromator because of the extremely high diffraction intensity and stability of this crystal under x-irradiation. A ground and elastically bent graphite crystal is used in the AMR-3-202 x-ray focussing monochromator used at DREP. The purpose of the

work discussed in this report has been to investigate and illustrate the various advantages of this accessory in the practice of x-ray diffractometry.

DESIGN AND FUNCTION OF THE X-RAY MONOCHROMATOR

In general, two considerations arise in the choice of the monochromator design to gain maximum efficiency, namely, the composition and preparation of the analyzing crystal, and the geometry of the monochromator. Also, several factors govern the selection of the crystal; for example, the crystal must possess high stability under x-irradiation, a low diffraction angle (low 2θ to minimize the polarization factor) and a high diffraction efficiency to minimize radiation losses by scattering and absorption of the x-ray beam. The relative diffracting power of the graphite (0002) crystal has been calculated (Renninger, 1956; Gould et al, 1968) to be approximately 620 as compared to 93 for the LiF (200) and 43 for the quartz ($10\bar{1}1$) crystals. Thus, graphite is the most efficient crystal monochromator presently available, since only small losses of intensity, relative to partially monochromatic methods, should occur. With regard to the geometrical arrangement of the monochromator, four alternative diffractometer geometries are possible, since the specimen and the crystal may be employed in either reflection or transmission. Each of these has been studied in detail by Lang (1956), who demonstrated that the reflection specimen-reflection crystal (RR) design could cover a wide range of 2θ angles without modification of the original diffractometer geometry. The transmission specimen-reflection crystal (TR) geometry gives the advantage of greater efficiency at 2θ angles lower than 30°, while the RT arrangement was able to record back-reflection angles with increased accuracy for lattice parameter determinations.

Figure 1 is a schematic of the conventional Bragg-Brentano diffractometer, and Figure 2 indicates how this geometry is modified by the addition of the monochromator. In the latter design, both the specimen and the crystal are reflecting surfaces; therefore, the practical range of the diffractometer (approximately 10° to 165° 2θ) is the same as that of a conventional Bragg-Brentano geometry. Only two parameters must be determined to isolate a particular wavelength. The distance, D, measured from the receiving slit to the crystal rotational axis must be adjusted according to the relation $D = R \sin\theta = R/2d\ \lambda$, where R is the radius of curvature of the crystal, d is the crystal spacing and λ is the wavelength to be isolated.

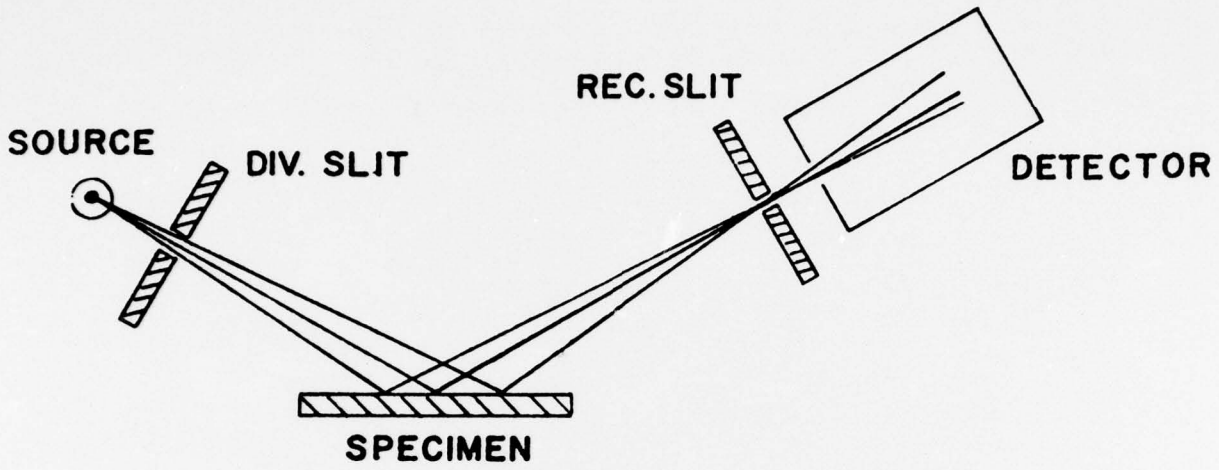
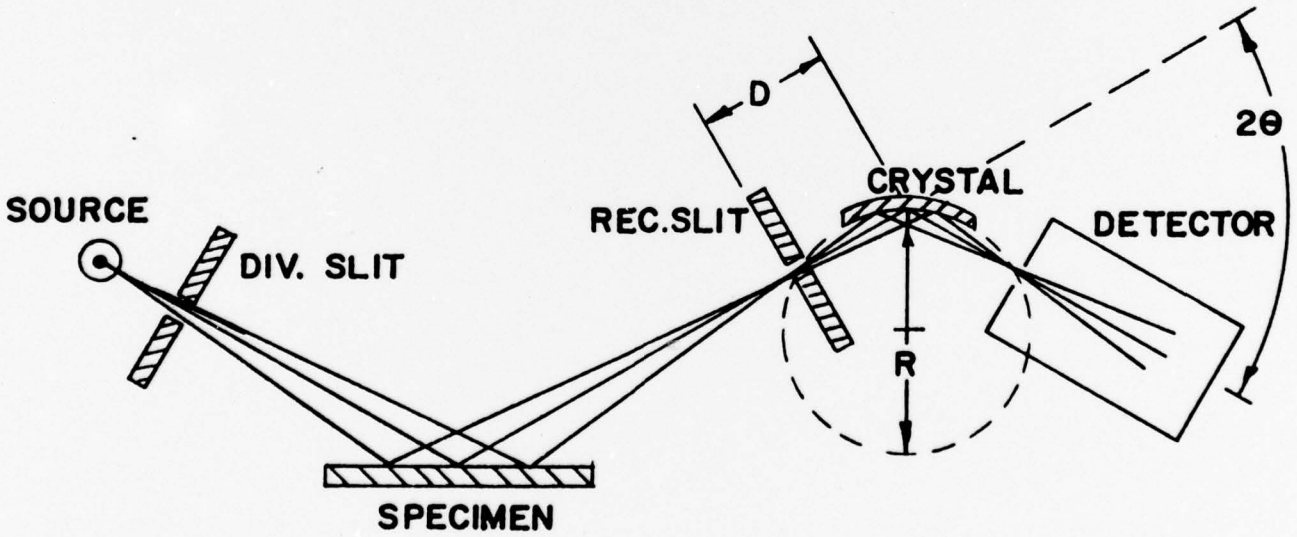

REC. SLIT
SOURCE
DIV. SLIT
DETECTOR
SPECIMEN

Fig. 1


D
2θ
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SPECIMEN

Fig. 2

Minute adjustments to the angle 2θ, i.e. the angle subtended by the incident and diffracted x-ray beams of the crystal, are necessary to gain maximum intensity. This arrangement differs from that of Lang only by the removal of the slit between the crystal and detector. This should result in an increased bandwidth of the monochromator due to lack of focussing, but with a subsequent increase in signal intensity.

Discrimination against all wavelengths except the $K\alpha$ doublet of the detected radiation removes all of the spurious lines and background that would otherwise complicate or distort the x-ray diffraction pattern. The monochromator should therefore provide the following advantages to the conventional x-ray diffractometer:

1). Discrimination against fluorescence and scattering of the primary x-ray beam by the sample.

2). Discrimination against the $K\beta$ line and continuous radiation (Bremsstrahlen). (This eliminates the need for β filters or other means of partial monochromatization of the primary x-ray beam.)

3). Provision of a shield against direct exposure of the detector to radiation produced as a result of radioactive decay of the sample, thus enabling the x-ray diffraction study of radioactive compounds.

4). Discrimination against radiation produced by impurities in the target material of the x-ray tube.

Of these, discrimination against specimen fluorescence is probably the greatest asset to x-ray diffractometry, since a high background can be produced if the incident radiation causes the excitation of secondary radiation in the sample. This will occur if the K absorption edge of the fluorescing element occurs at a slightly longer wavelength than the $K\alpha$ line of the exciting radiation. Fluorescence is at a maximum, therefore, if the atomic number (Z) of the fluorescing element is two or three lower than that of the x-ray tube target material, For example, it is difficult to observe patterns of Fe-containing compounds with Cu radiation without monochromatization of the diffracted beam because of high background fluorescence. In order to overcome this, it is usually necessary to have a variety of x-ray tubes available and to choose a radiation source that is compatible with the specimen material. This practice is both costly and time-consuming, and is unnecessary if a monochromator is employed, since one radiation source may be used regardless of specimen composition.

INSTRUMENTATION.

The diffractometer consists of a Philips wide range vertical goniometer (PW 1050) fitted with a scintillation detector. The x-ray tube and associated electronics are supplied by a 60 kV generator (PW 1140/00), while signal processing (pulse height analysis) is accomplished by a Philips PW 1370 electronic measuring panel and recorder. The following instrumental parameters were used for the selection of the various pulse amplitudes:

	CuKα	Fe Kα	Cr Kα
Detector potential*	260	225	235
Window*	360	320	360
Lower level*	270	150	140
Attenuation	2^3	2^2	2^2

* Helical potentiometer units - continuously variable through 0 to 1000 range.

Complete diffraction patterns were recorded with the following settings:

2θ Range	-	10° - 90°
Tube potential	-	40 kv
Tube current	-	20 mA
Scan speed	-	1°/min
Chart speed	-	10 mm/min
Take-off angle	-	6°
Divergence slit	-	1°
Receiving slit	-	0.2 mm (without monochromator)
	-	¼° (with monochromator)
Scatter Slit	-	1° (without monochromator)
	-	none (with monochromator)

X-ray monochromatization is accomplished with a bent graphite crystal monochromator supplied by the Advanced Metals Research, Burlington, Mass. (Model AMR-3-202).

RESULTS AND DISCUSSION

The characteristics of the x-ray monochromator were investigated to illustrate its two most important functions; elimination of Kβ and other spectrum lines, and discrimination against sample fluorescence and scattering. Each of these effects may be demonstrated by visual comparison of diffraction scans taken with and without the monochromator. The degree to which the monochromator is effective should also be evident by an increased signal-to-noise ratio (S/N) as defined by:

$$S/N = \frac{I_P - I_B}{I_B}$$

where I_p and I_B are the peak and background intensities of a major diffraction line, respectively.

(a) Discrimination Against Undesired Spectrum Lines.

Figure 3 compares, respectively, the (321) reflection of tungsten using Cu radiation

1). with the monochromator

2). with a Ni beta filter, and

3). with no monochromatization, that is, without the graphite monochromator or Ni filter.

Although visually the line profiles are very similar, some decrease in background is exhibited by the use of a beta filter and it is still further decreased by the monochromator. The salient feature of the monochromator is the elimination of Kβ and other spectrum lines from the diffracted beam without significant intensity loss. Thus, the need for a beta filter or other form of partial monochromatization is eliminated. The advantage of the crystal monochromator is verified by the increased S/N ratios for the W (321), Si (311), and other reflections, as shown in Table I. These increased S/N ratios indicate a significant reduction of background with the monochromator relative to a simple beta filter or a polychromatic beam.

Table I Signal-to-Noise Ratios of Selected Diffraction Lines

Specimen	Radiation Source	2θ	Without Filter	With Filter	With Monochromator
Tungsten (321)	Cu	131.11°	7.3	17.1	40.3
Silicon (311)	Cu	56.12°	20.4	26.4	39.4
Fe_2O_3	Cu	33.26°	-	1.0	45.9
$CoCl_2 \cdot 6H_2O$	Cu	15.79°	-	1.2	13.5
$Na_3Fe_3(SO_4)_3$	Cu	28.31°	-	3.1	26.5
V_2O_5	Fe	25.70°	8.3	20.3	203.9
$CrCl_3$	Fe	20.85°	1.2	1.9	63.8
$MnSO_4$	Fe	32.16°	7.0	8.6	44.0
V_2O_5	Cr	30.47°	21.1	26.0	123.0
TiO_2	Cr	38.10°	1.6	2.6	80.2

(b) Discrimination Against Specimen Fluorescence.

As seen from the diffraction pattern of α-Fe_2O_3 (hematite) with Cu Kα radiation (Figure 4), an extremely high background, caused solely by fluorescent radiation emitted from the sample, is produced. This background must be reduced before accurate measurements of the line positions and their relative intensities can be accomplished. Many of the less intense lines may also be distorted or completely masked by the background. Figure 5 shows the diffraction pattern of the same specimen measured with the monochromator in place. The background is virtually eliminated except at very low diffraction angles ($\simeq 10°$). However, the high background at low 2θ angles is an effect of the slit arrangement, and is not due to fluorescent radiation. The resolution of the diffractometer is improved somewhat, since the Kα doublet is partially resolved for some high-angle reflections. The reduction of background is also exhibited by an increase of the S/N ratio of the strongest diffraction line for Fe_2O_3 (occurring at 33.26° 2θ with Cu Kα) from 1.0/1 with a Ni beta filter to 459/1 with the monochromator. Table I lists the S/N ratio determined in each of the three modes for a variety of compounds for which the combination of elemental constituents and incident radiation is particularly efficient for the excitation and fluorescence. Since the background produced is proportional to the concentration of the fluorescing element present, the degree of improvement in S/N ratio may vary, but in each instance there is virtual elimination of fluorescence background. Figures 6-11 give further visual evidence of the effectiveness of the monochromator, in contrast to β filters, for the relief of this background, regardless of the radiation used. The beneficial effect of the monochromator will be less pronounced in some scans than in others because of differing full scale deflections of the rate meter.

SOME PRACTICAL APPLICATIONS.

By the nature of many analytical problems encountered at DREP, it is often necessary to identify compounds present in mixtures of materials or compounds which have a complex crystal structure. This necessitates the

accurate measurement of the diffraction pattern to positively identify many of these compounds. Frequently, this is only possible if the diffraction pattern is well-defined and free from distortion. In the course of several analyses associated with ship engineering problems, many compounds have been identified by the x-ray diffraction technique, but two examples may be given to illustrate how the application of the monochromator in x-ray diffractometry has facilitated analysis.

(a) Fireside Deposits in DDE Main Boilers

DREP has undertaken experimental studies to identify and characterize deposits remaining in the main boilers of DDE class ships (Dominique & Waggoner, unpublished data, 1975). The presence of $Na_3Fe(SO_4)_3$ in these deposits was indicated by the x-ray diffraction technique, and subsequently confirmed following the laboratory synthesis of this compound. Since this and other Fe-containing compounds were identified as components of the deposit mixture, it was deduced that significant corrosion of the fire-row tubes and other exposed surfaces could occur during boiler operation.

Accurate measurement of the diffraction pattern of the synthesized salt, $Na_3Fe(SO_4)_3$, is most easily accomplished by the diffractometric technique. Figures 12 and 13 show respectively, the diffraction patterns obtained by Cu Kα radiation with a beta filter and with the crystal monochromator. Many features of the diffraction pattern are visible only by the removal of background radiation by the monochromator. In a similar manner, Figures 14 and 15 compare the diffraction patterns of the untreated deposit obtained from the main boiler of HMCS PROVIDER. Although the patterns look very similar and the lines appear stronger in the scan made with the Ni beta filter, only a few lines are representative of the $Na_3Fe(SO_4)_3$. Positive identification of this compound was possible only by accurate measurement of the very weak lines of the compound, which were more clearly defined in the pattern obtained by using the monochromator. Another compound, probably another form of sodium sulfate, appears to be the principal component of the deposit.

(b) "Chrome Ore" Refractory

"Chrome ore" has frequently been employed as a pliable refractory compound for use in DDE main boilers. This compound is essentially chromite, $FeCr_2O_4$, but inclusions of Al and Mg may occur. The diffraction patterns of dried "chrome ore", shown in Figures 16 and 17 indicate that the specimen is essentially pure, and does not contain the aluminum or magnesium forms. Diffraction lines of low relative intensity are elucidated by use of the monochromator, thus allowing the positive identification of very weak lines, and the possible detection of minor compounds.

SUMMARY.

The graphite crystal monochromator is effective in x-ray diffractometry for the elimination of all wavelengths other than the Kα doublet of the radiation source. This results in decreased background caused by scattering and specimen fluorescence and the elimination of undesirable lines and continuous radiation of the x-ray spectrum. The observed benefits are an increased S/N ratio and visual clarity of the x-ray diffraction pattern, thus allowing increased accuracy of detection and measurement of diffracted line positions and their relative intensities.

Although all of the examples discussed above involve qualitative analysis, i.e. identification of a compound or a mixture of compounds, quantitative and semi-quantitative analyses may also be accomplished by the diffractometric technique. The benefits provided by the monochromator should be of even greater importance in this application, since maximum peak intensity and a minimum of associated background are necessary for accurate and reproducible analysis.

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M. Renninger, Z. Kristallogr., 107, 464, (1956)

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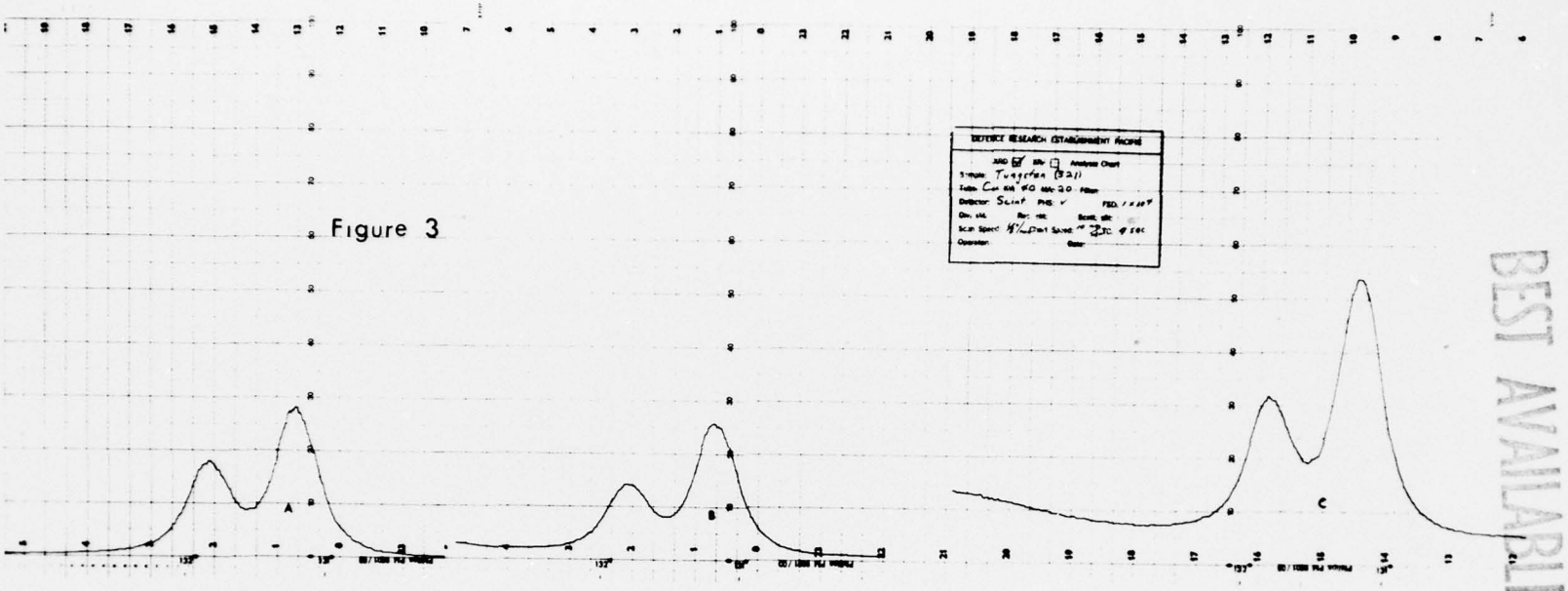
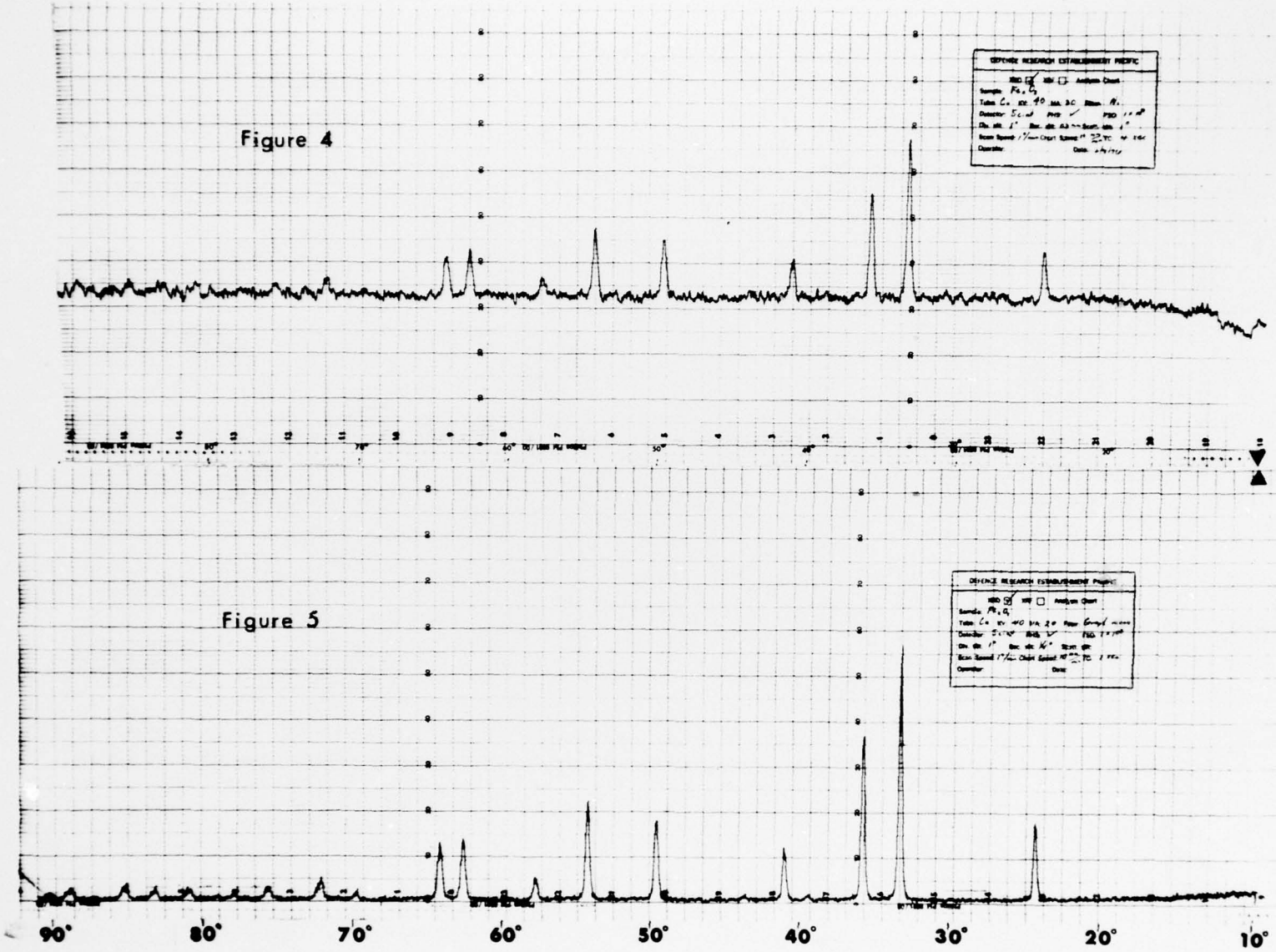
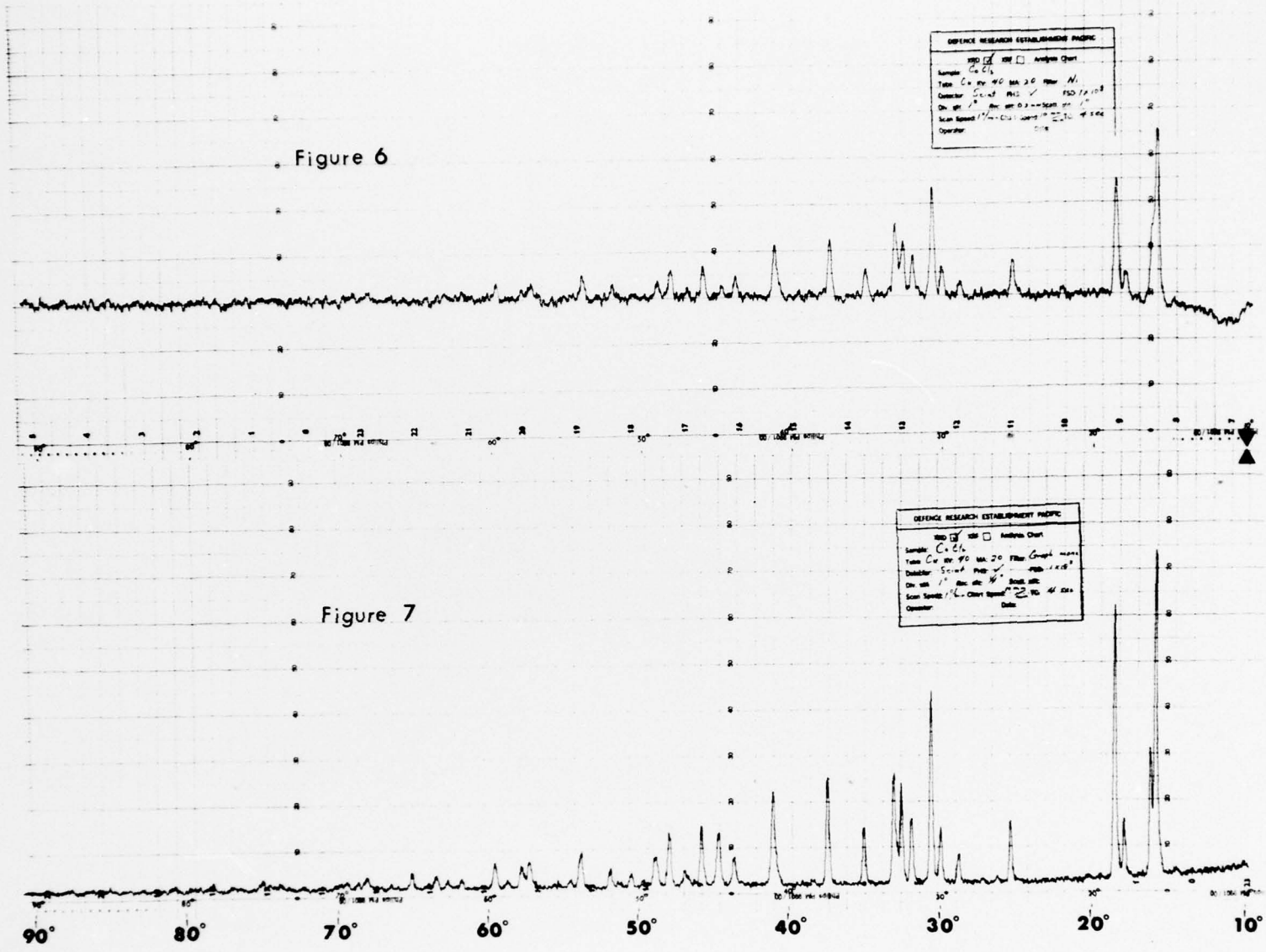


Figure 3 Tungsten (321) Reflection - Cu Kα

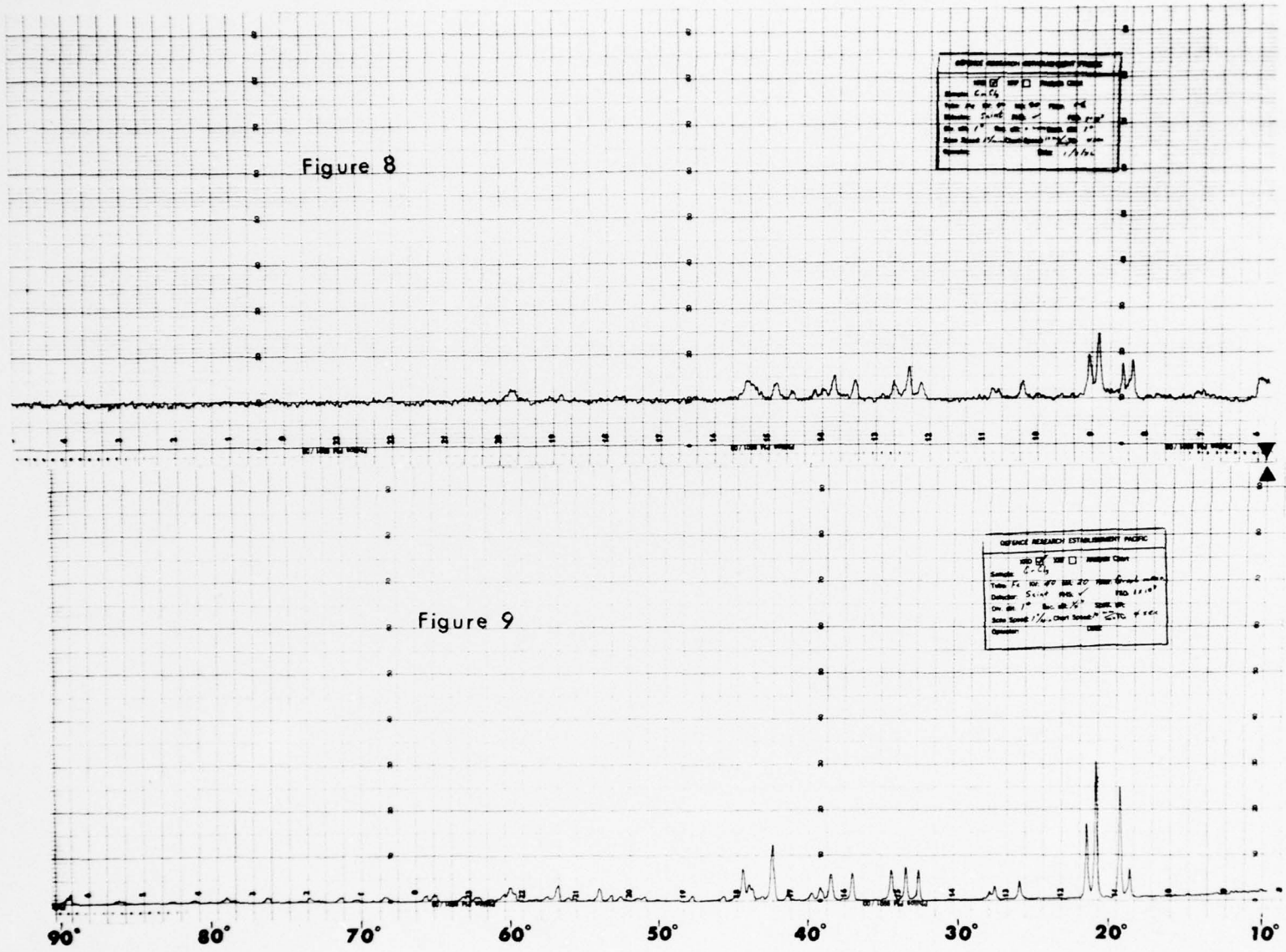
A. with monochromator
B. with Ni β-Filter
C. without monochromator



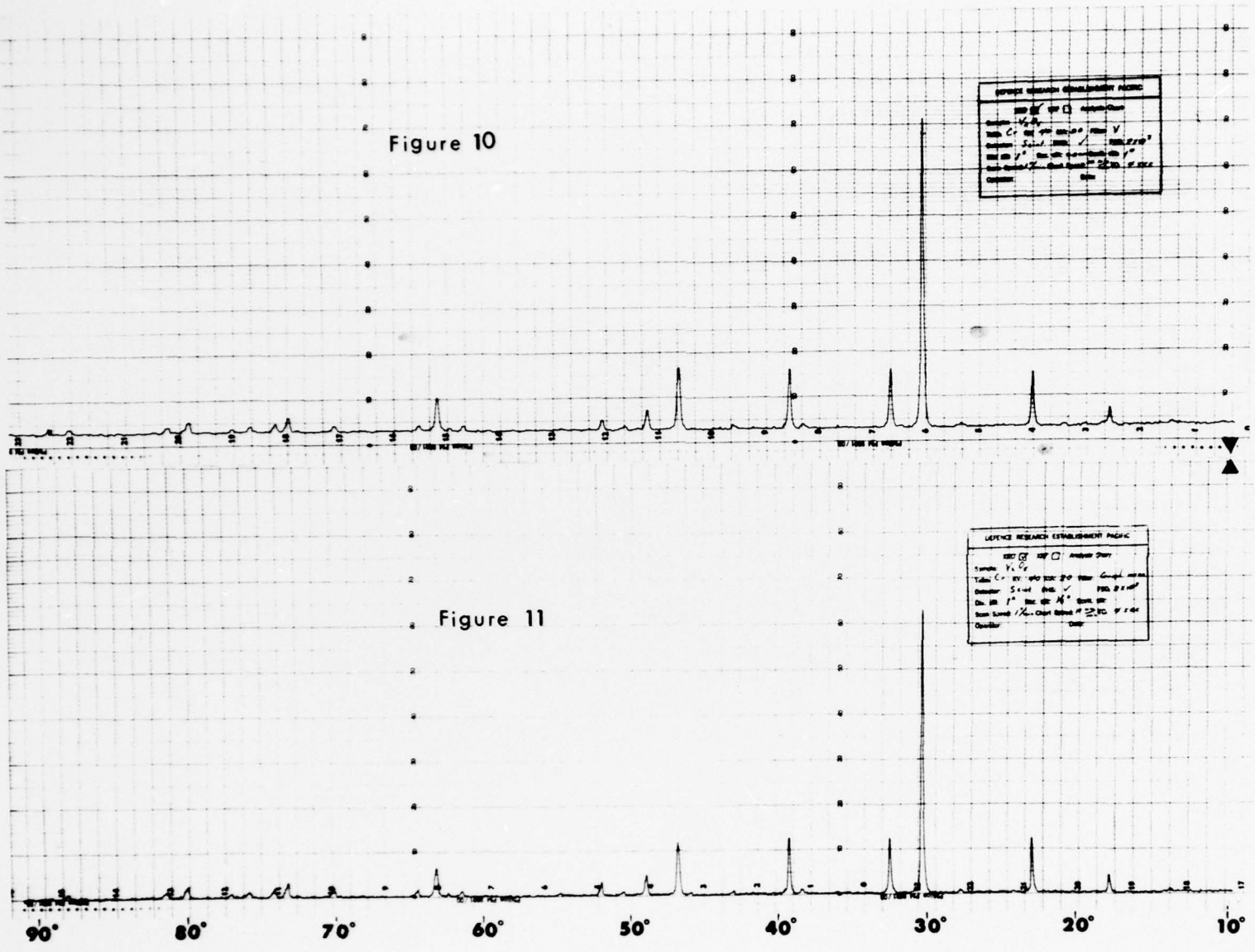
XRD Patterns of Fe_2O_3 : Figure 4 - without monochromator
Figure 5 - with monochromator



XRD Patterns of $Co\,Cl_2$: Figure 6 - without monochromator
Figure 7 - with monochromator



XRD Patterns of $CrCl_3$: Figure 8 - without monochromator
Figure 9 - with monochromator



XRD Patterns of V_2O_5 :

Figure 10 - without monochromator
Figure 11 - with monochromator

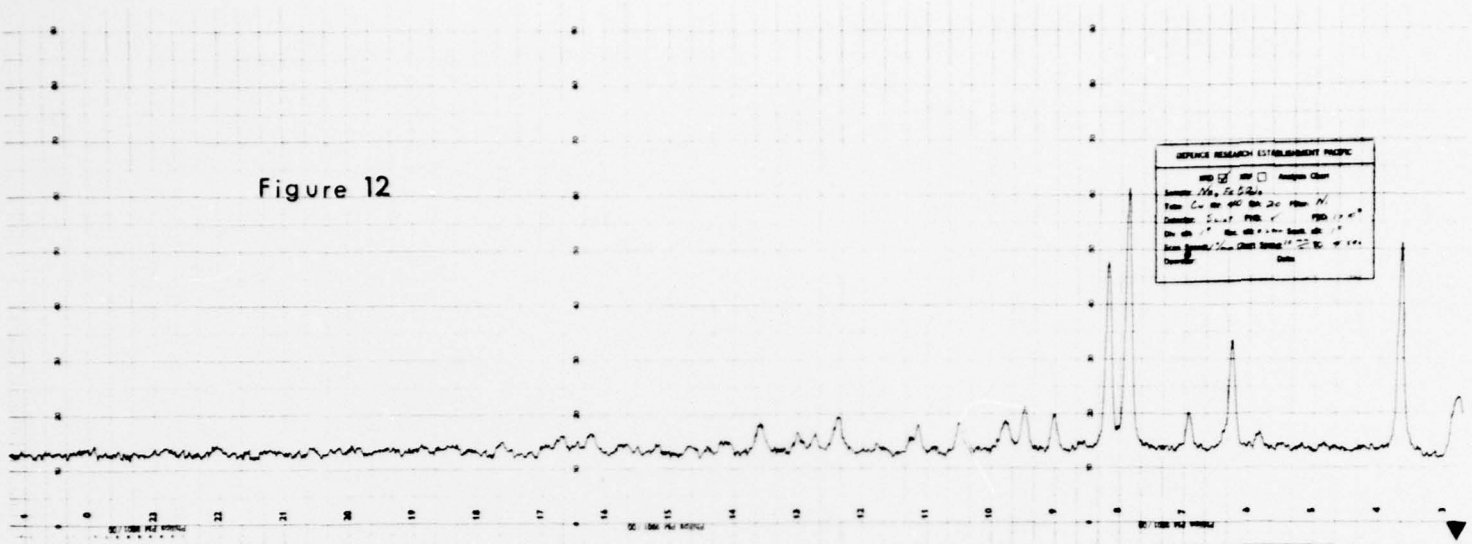


Figure 12

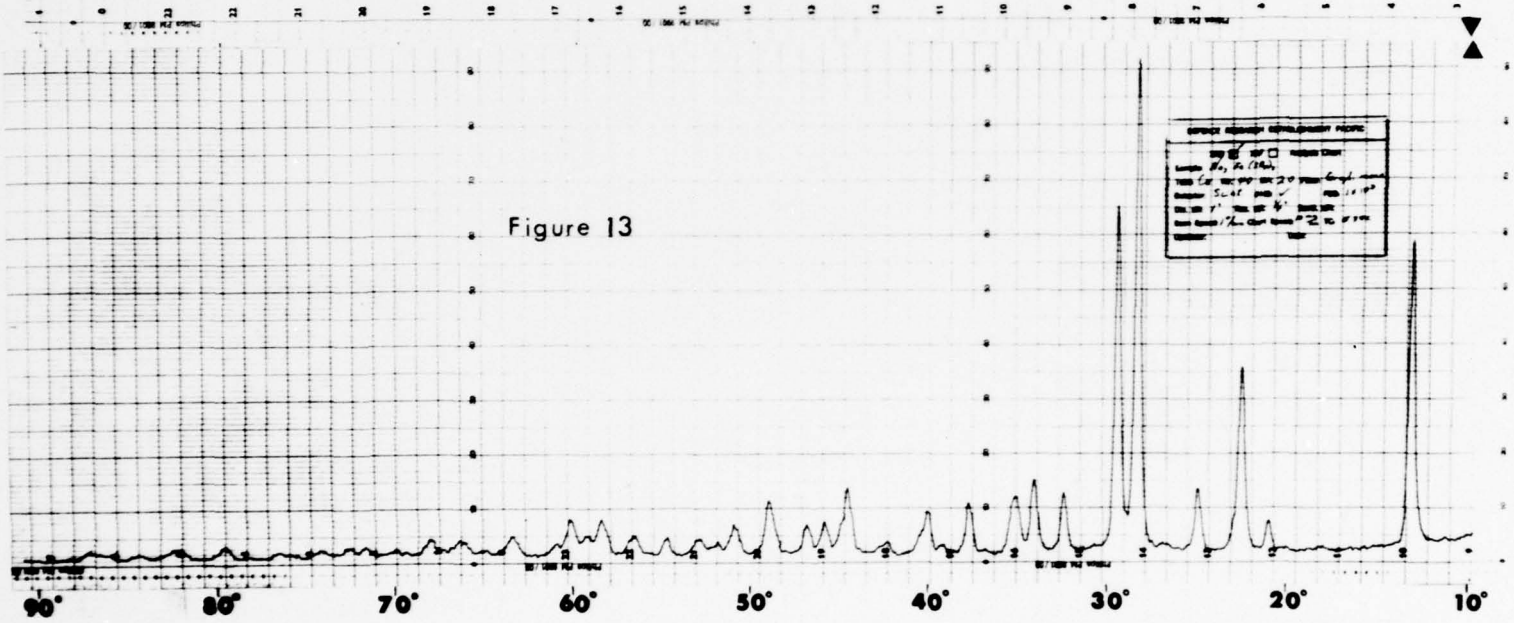
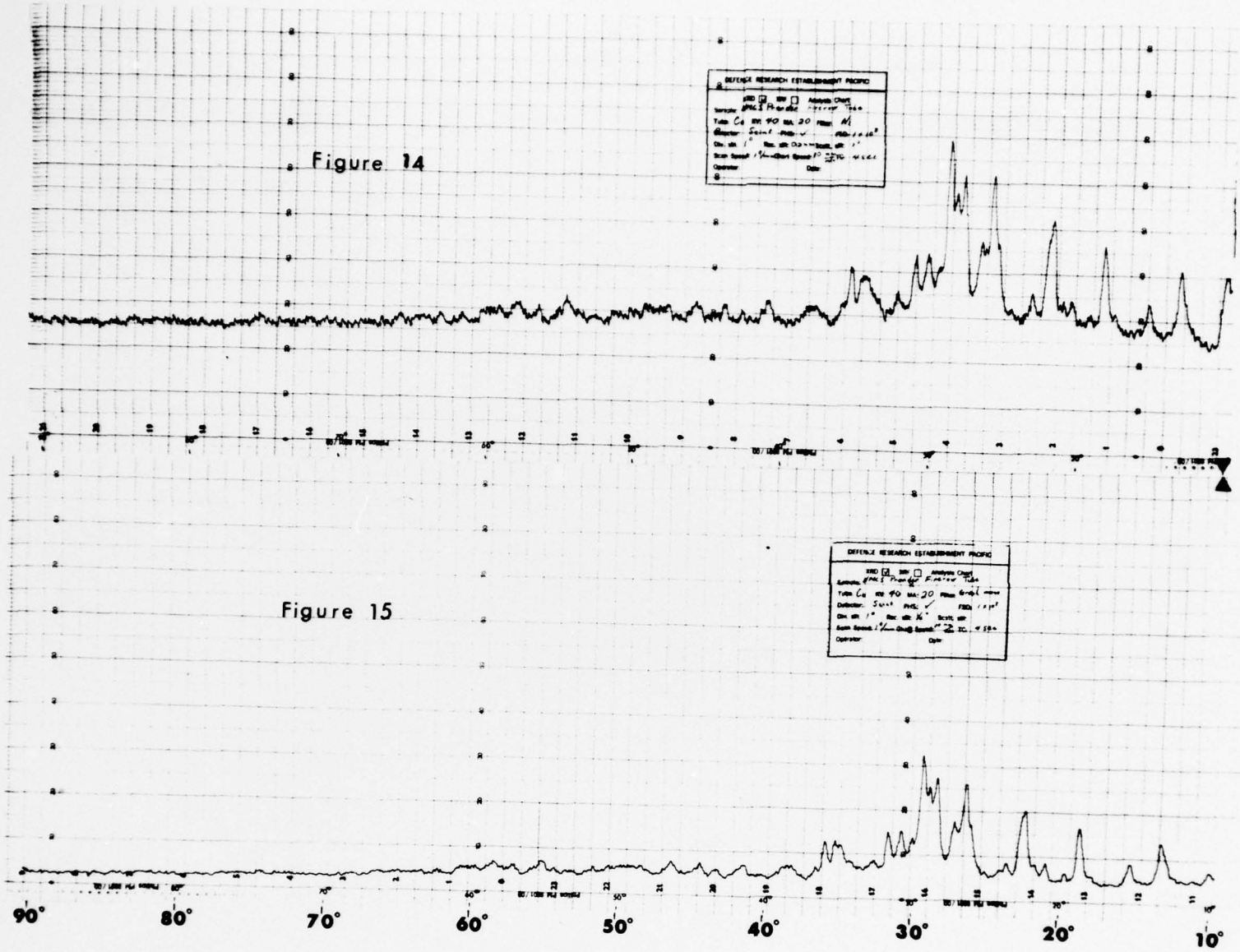


Figure 13

XRD Patterns of $Na_3 Fe (SO_4)_3$: Figure 12 - without monochromator
Figure 13 - with monochromator



XRD Patterns of Firerow Tube Deposit : Figure 14 - without monochromator
Figure 15 - with monochromator

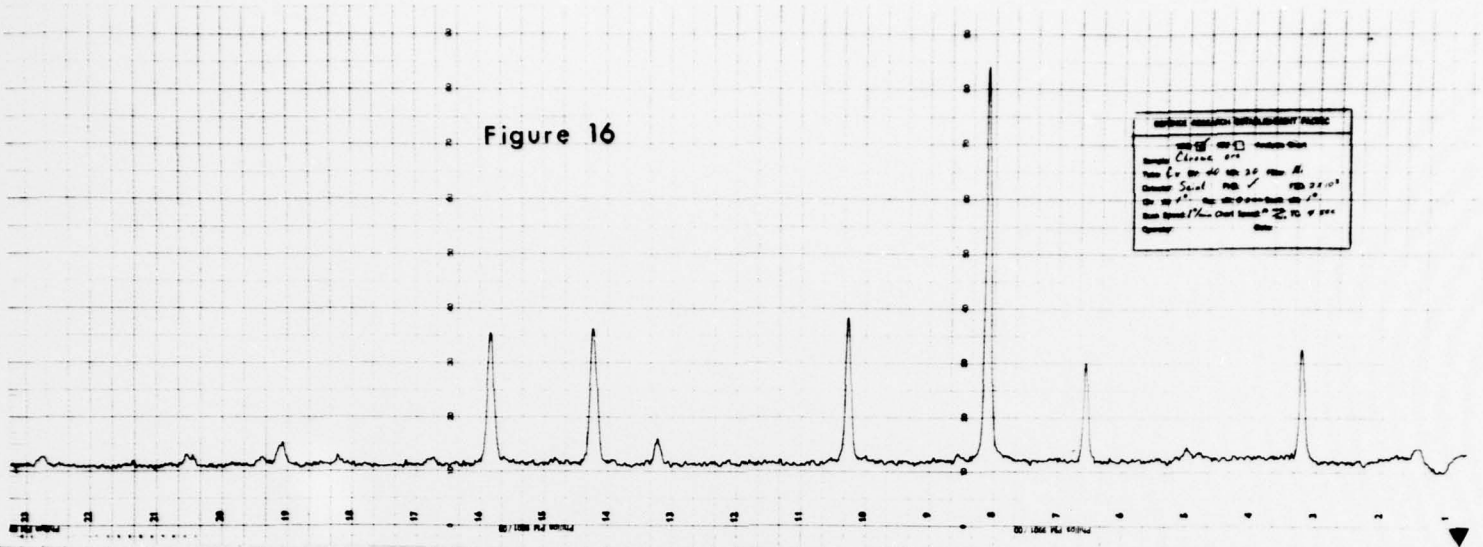


Figure 16

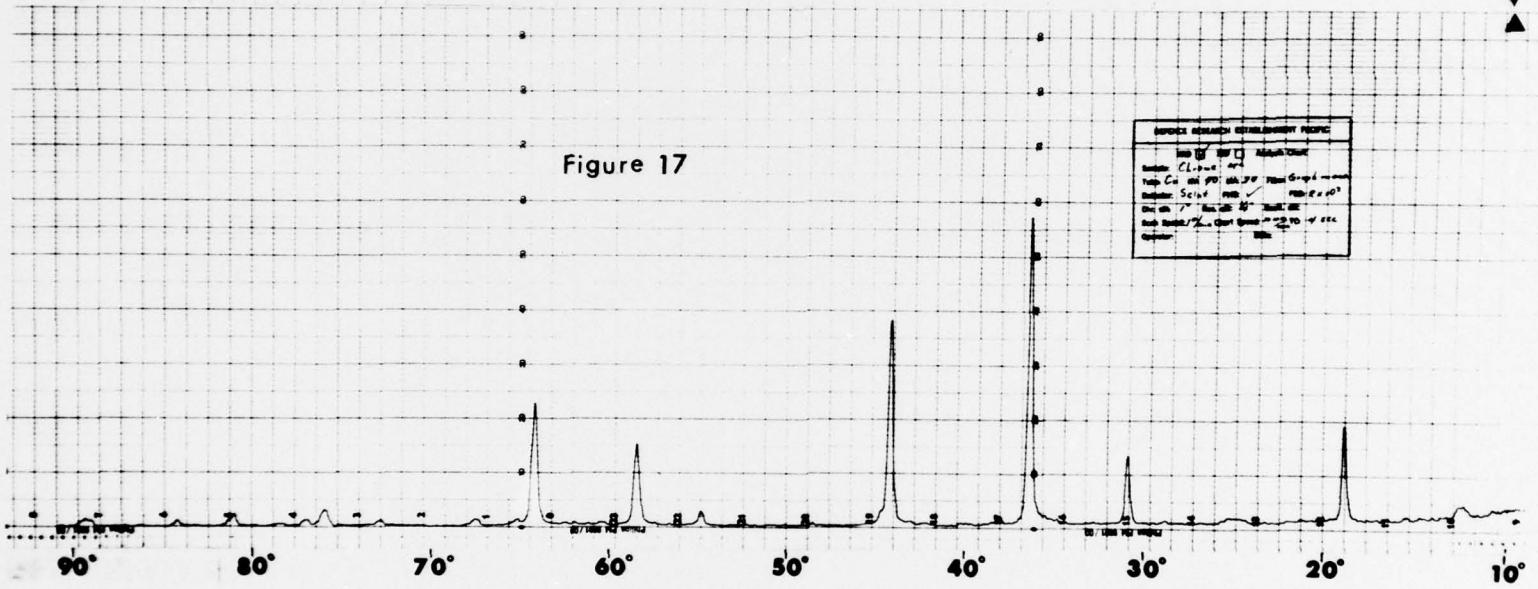


Figure 17

XRD Patterns of "Chrome Ore" : Figure 16 - without monochromator
Figure 17 - with monochromator